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Abstract

The previous studies of La Mer et al on the flocculation of fine quartz dispersions with ionic polymers, as measured by refiltration rates and electrophoretic mobilities, supported by U.S.P.H.S. Grants, are being continued. Emphasis is now being placed on the effect of molecular weight and molecular architecture of cationic polymers on flocculation phenomena. Polyalkylene amines, for example, triethylene tetramine and polyethylene imine, with molecular weights ranging from 150 to 75,000 have been studied. As the molecular weight of the polymer decreases from 75,000 to 3,000 the refiltration rate through the quartz is but little affected by the molecular weight. However, as the molecular weight decreased from 3,000 to 150-200 the refiltration rate decreased markedly. Polymers are being prepared with molecular weights between 200 and 3,000 in order to obtain information in this important region. Attempts will be made to determine molecular weights in this range by freezing point and viscosity measurements.

The electrophoretic mobility varies with concentration of added cationic polymer, changing from (-) to (+) in a concentration range which is qualitatively near that at which refiltration rate is a maximum; however, the mobility may still be strongly negative or positive where the refiltration rate is also still large.

Polyethylene imine polymers with molecular weights of 45,000 to 75,000 show very poor refiltration rates at concentrations above 5-15 ppm by weight, but in this region flocculation and settling are rapid. Further study of this phenomenon as a function of molecular weight may be important.

I. Experimental

A. Cationic Polymers Tested

		Molecular Wt.*
Triethylene tetramine (TETA)	$H_2N(CH_2CH_2NH)_2\ CH_2CH_2NH_2$	146
Tetraethylene pentamine (TEPA)	$H_2N(CH_2CH_2NH)_3\ CH_2CH_2NH_2$	189
Polyethylene imine (Dow) SA 1117	$CH_2\text{-}CH_2$ (N, H) $(CH_2CH_2NH)_x CH_2CH_2NH_2$	3,000
Polyethylene imine (Dow) NC 1105		45,000
Polyethylene imine (Dow) ET 494		75,000
Polyethylene imine (Dow) ET 723		75,000

* Molecular Weights supplied by the Dow Chemical Co.

B. Crystalline Quartz

Studies of flocculation were made on crystalline quartz, Min-U-Sil "5μ", "10μ" and "15μ" nominal sizes of the Pennsylvania Glass Sand Co., which have average particle diameters of 1.1μ, 2.1μ and 2.7μ, respectively, measured by the supplier using the Blaine Air Permeability Apparatus.

C. Refiltration Tests

The refiltration method used by Kane, La Mer and Linford (J. Phys. Chem., 67, 1977 (1963)) has been used, which measures the time to refilter 50 cc. of filtrate through the quartz filter cake. The rate has been found to be influenced to some extent by (a) the amount of filtrate run through the filter cake, (b) whether the vacuum applied during filtration is broken and then re-established and, (c) to a considerable extent by the type of filter paper used as the support for the cake. The difference between the refiltration rate for

the quartz with and without added polymer, is dependent to some extent on the filtration resistance of the filter paper.

D. Electrophoretic Mobility Measurement Method

See the paper of La Mer et al (J. Am. Chem. Soc., 86, 3450 (1964) in which the "Zeta Meter" was used. In order to measure electrophoretic mobility and filtration on corresponding dispersions, a concentrated solution of silica, usually 5 g./300 cc., was treated with polymer, an aliquot was taken out and diluted with filtrate from the remainder until the silica concentration was low enough to permit electrophoretic mobility measurement. Filtration rate was measured on the undiluted dispersion.

Measurements of electrophoretic mobility on silica particles are made in the cylindrical cell of the Zeta Meter. Since the particles settle rapidly after addition of a flocculant, velocity measurements are made on those particles which may not be representative of the major part of the solid which settles rapidly to the bottom of the cell. This problem is also typical of that encountered in the Briggs cell used by A. P. Black and others, and will receive more adequate attention in the future.

E. Adsorption of Polymer on Silica

The adsorptions of polyalkylamines were determined by titration of the solution before and after treatment with silica. At 5 g. of SiO_2/300 cc. solution, the percentage adsorptions of TETA and TEPA were too small to be measured by this differential titration procedure. However, Polymer S1117, the lowest molecular weight polyethylene imine, was adsorbed to an extent of 50 to 80% at added concentrations of 25 to 100 ppm by weight. Obviously,

adsorption of S1117 polymer with molecular weight of 3000 reduces the weight concentration by a much greater percentage than adsorption of the same number of molecules of TETA or TEPA.

For a low "polymer" like TETA the area of "5μ" nominal quartz is 0.3 to 13 times the area of the polyamine at 0.04 to 1.66 g. silica per 100 cc., respectively. See Table I which follows.

TABLE I

Comparison of Areas of Polymer and Silica ("5μ" Nominal Size)

Concn. of SiO_2, g./ 100^{-}cc.	Wt.ppm polymer in solution.	Mol. Wt. Polymer.	Vol. of SiO_2, cc. per cc. solution	No. of particles per cc. solution.		Area in cm^2 per cc. solution.	
				SiO_2	Polymer	SiO_2	Polymer
0.04	1.0	43	$1.5x10^{-4}$	$2.14x10^{8}$	$14x10^{15}$	8	25
1.66	1.0	43	$62.1x10^{-4}$	$89x10^{8}$	$14x10^{15}$	330	25
0.04	1.0	10,000	$1.5x10^{-4}$	$2.14x10^{8}$	$6x10^{13}$	8	$1.1x10^{-1}$
1.66	1.0	10,000	$62,1x10^{-4}$	$89x10^{8}$	$6x10^{13}$	330	$1.1x10^{-1}$

If, however, a high polymer of molecular weight 10,000 is adsorbed and the area occupied by each polymer molecule is equal to that of one polymer segment (about $18A^2$), then the silica area is some 80-3300 times the area which the polymer can occupy. Adsorption soon depletes the polymer concentration in solution so that the amount of adsorption can be determined by titration.

II. Refiltration Results

Refiltration curves for "5μ" nominal size silica at pH-4.0 and 9.0 for TETA, TEPA ET 723, ET 494, NC1105 and SA1117 are shown in Figures 1-3, at concentrations from 0.1 to 1000 ppm. Note that refiltration time which is shown is the reciprocal

FIGURE 1

Effect of Concentration of Cationic Polymer On

Refiltration Time of Crystalline Quartz of "5μ" Nominal Size.

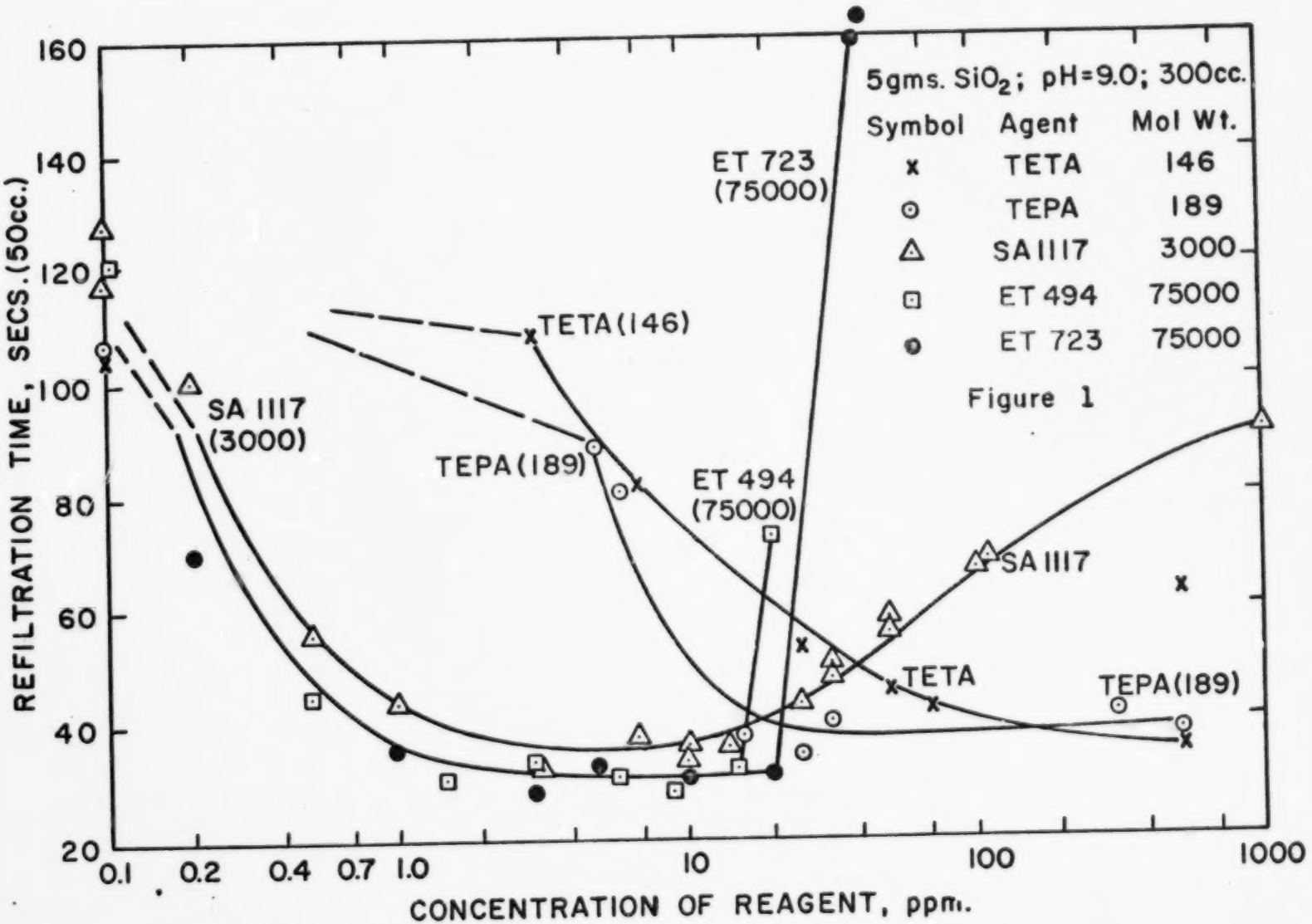
5gms. SiO2; pH=9.0; 300cc.
Symbol Agent Mol Wt.
x TETA 146
⊙ TEPA 189
△ SA 1117 3000
⊡ ET 494 75000
● ET 723 75000
ET 723 (75000)
TETA(146)
SA 1117 (3000)
TEPA(189)
ET 494 (75000)
SA 1117
TETA
TEPA(189)
REFILTRATION TIME, SECS.(50cc.)
160
140
120
100
80
60
40
20
0.1
0.2
0.4
0.7
1.0
10
100
1000
CONCENTRATION OF REAGENT, ppm.

Figure 1

FIGURE 2

Effect of Concentration of Cationic Polymer On

Refiltration Time of Crystalline Quartz of "5μ" Nominal Size.

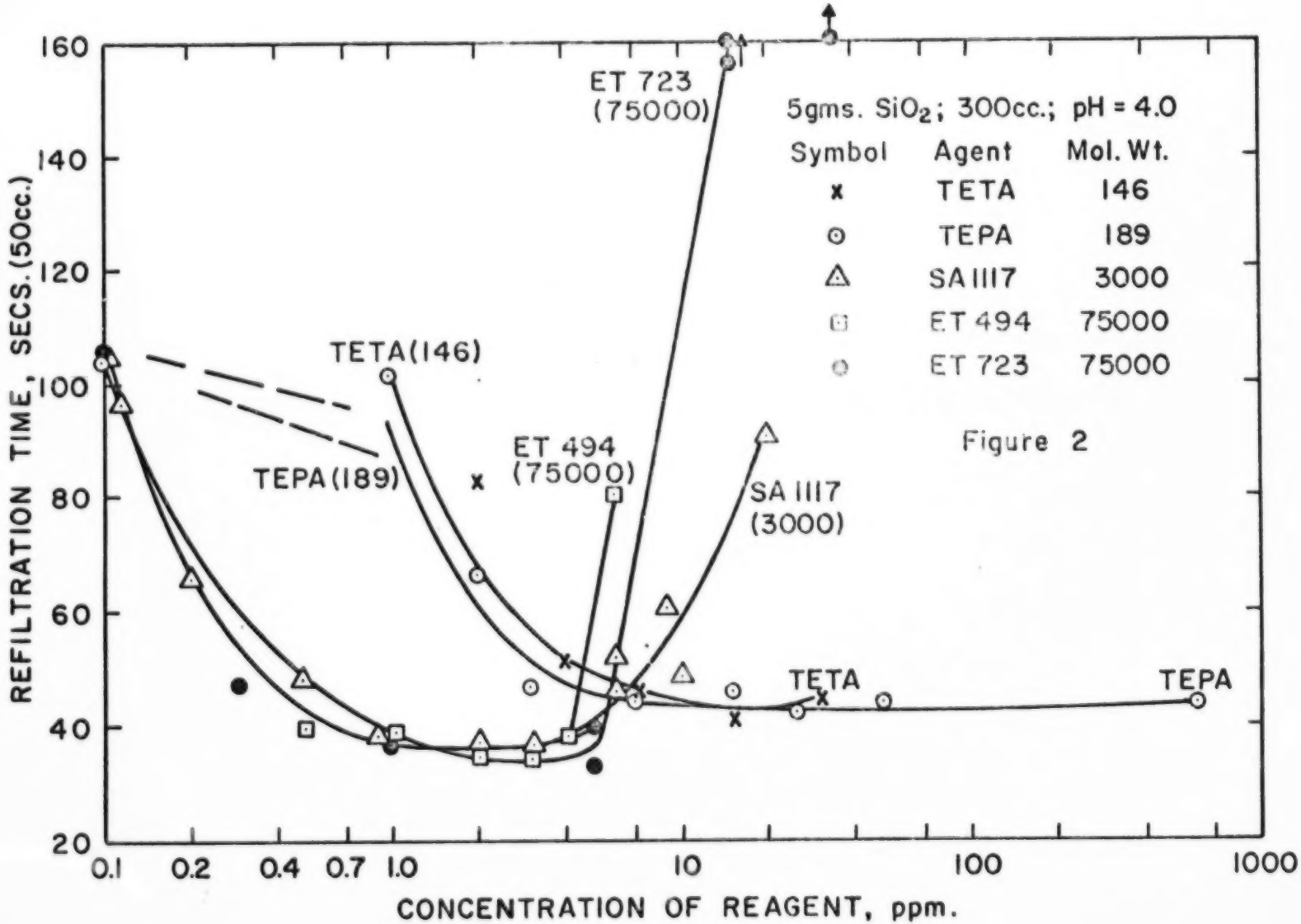
5gms. SiO_2; 300cc.; pH = 4.0
Symbol Agent Mol. Wt.
x TETA 146
⊙ TEPA 189
△ SA 1117 3000
⊡ ET 494 75000
○ ET 723 75000
ET 723 (75000)
TETA(146)
TEPA(189)
ET 494 (75000)
SA 1117 (3000)
TETA
TEPA
REFILTRATION TIME, SECS.(50cc.)
CONCENTRATION OF REAGENT, ppm.
160
140
120
100
80
60
40
20
0.1
0.2
0.4
0.7
1.0
10
100
1000

Figure 2

FIGURE 3

Effect of Concentration of Cationic Polymer On
Refiltration Time of Crystalline Quarts of "5μ" Nominal Size.

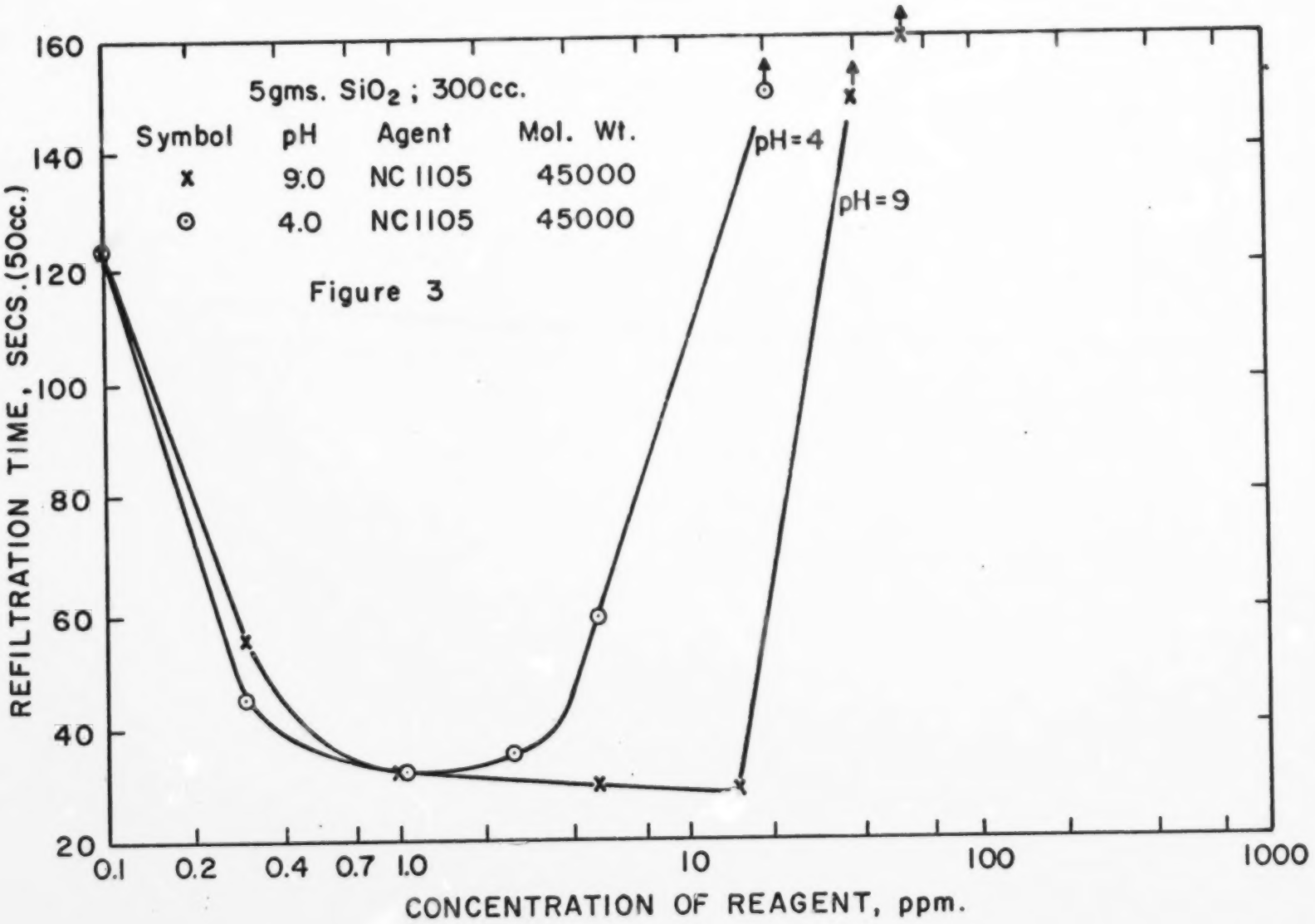
5gms. SiO2 ; 300cc.
Symbol pH Agent Mol. Wt.
x 9.0 NC 1105 45000
⊙ 4.0 NC1105 45000
pH=4
pH=9
160
140
120
100
80
60
40
20
REFILTRATION TIME, SECS.(50cc.)
0.1
0.2
0.4
0.7
1.0
10
100
1000
CONCENTRATION OF REAGENT, ppm.

Figure 3

of refiltration rate.

There is little effect of molecular weight from 75,000 down to 3,000 except at the latter value the rate does not show the critical decrease at the higher concentrations which is observed with the higher polymers. TETA and TEPA flocculate the quartz effectively, but at some 10-50 fold higher concentrations than the polyethylene imine polymers. The effect of pH is pronounced with TETA and TEPA, requiring a lower amount at pH 4.0 to maximize filtration rate, presumably because the polyamine is more positively charged at lower pH's. Also, with the higher polymers, a lower concentration is required at pH=4 to make the filtration rate decrease in a critical manner, even though the flocculation remains good. Polymer SA 1117 is an exception, because in the high concentration range where filtration rate decreases rapidly, the flocculation disappears and the quartz is redispersed.

III. Electrophoretic Mobility Results

Electrophoretic mobility results are plotted in Figures 4-6. Addition of TETA and TEPA changes the electrophoretic mobility from -2.0 up to $\pm$ 0.0 at 15-100 ppm. The curves for pH=4 and 7.0 are about the same, but at pH 9.0, a higher concentration of polymer is required to reverse the charge, probably because a larger fraction is in the unprotonated form of the basic polymer. The same behavior appears to be the case for the higher polymers, ET 494, ET 723, and SA 1117. In Figure 6 it will be noted that the concentration of polymer required to reverse the charge is less for quartz with nominal size "15μ" than it is for the nominal size "5μ". This would be expected on the basis of a two-fold smaller area of the larger size.

FIGURE 4

Effect of Concentration of Cationic Polymer On Electrophoretic Mobility of Crystalline Quartz of "10μ" Nominal Size.

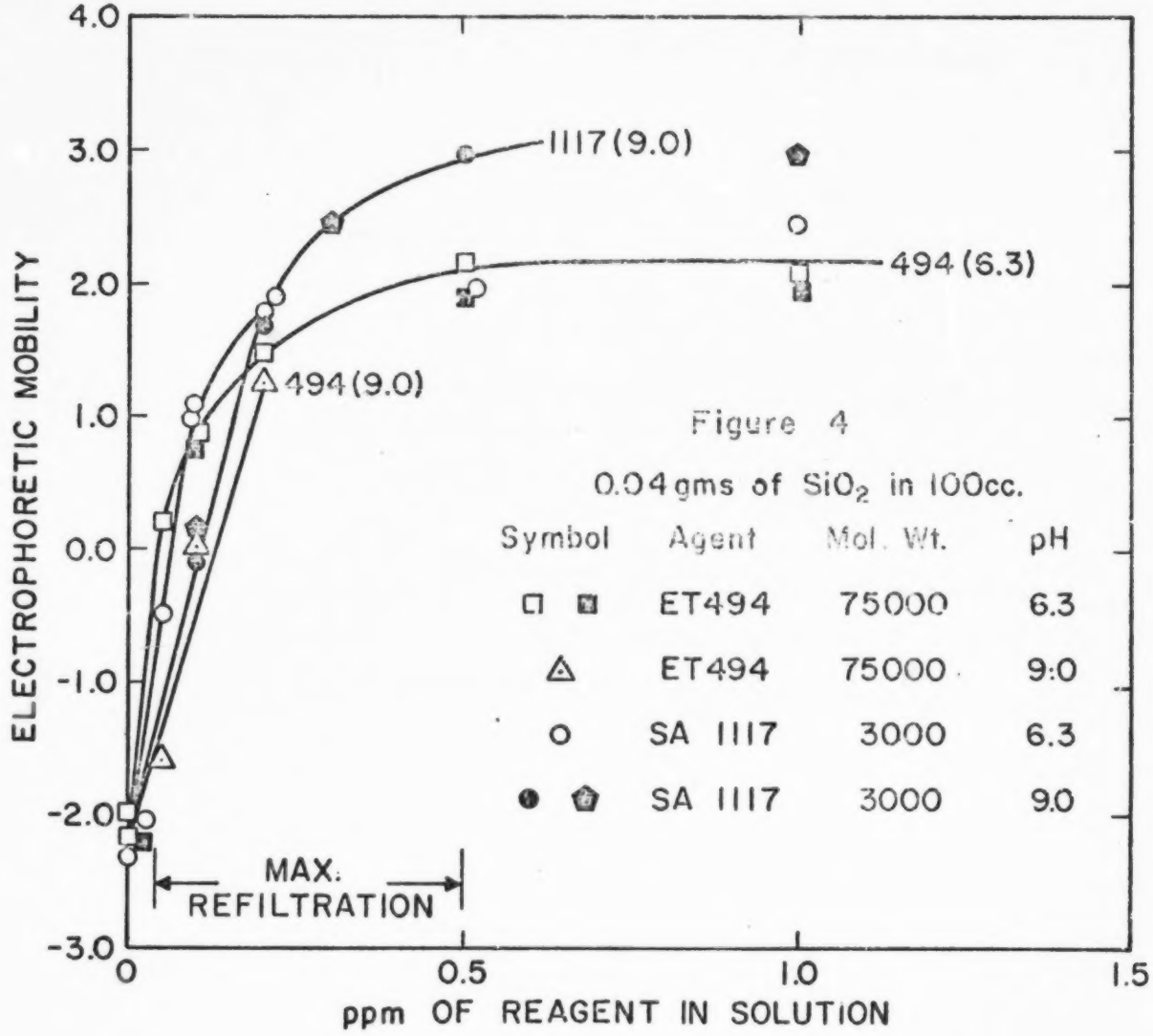

Figure 4

0.04 gms of SiO_2 in 100cc.

FIGURE 5

Effect of Concentration of Cationic Polymer On
Electrophoretic Mobility of Crystalline
Quartz of "10μ" Nominal Size.

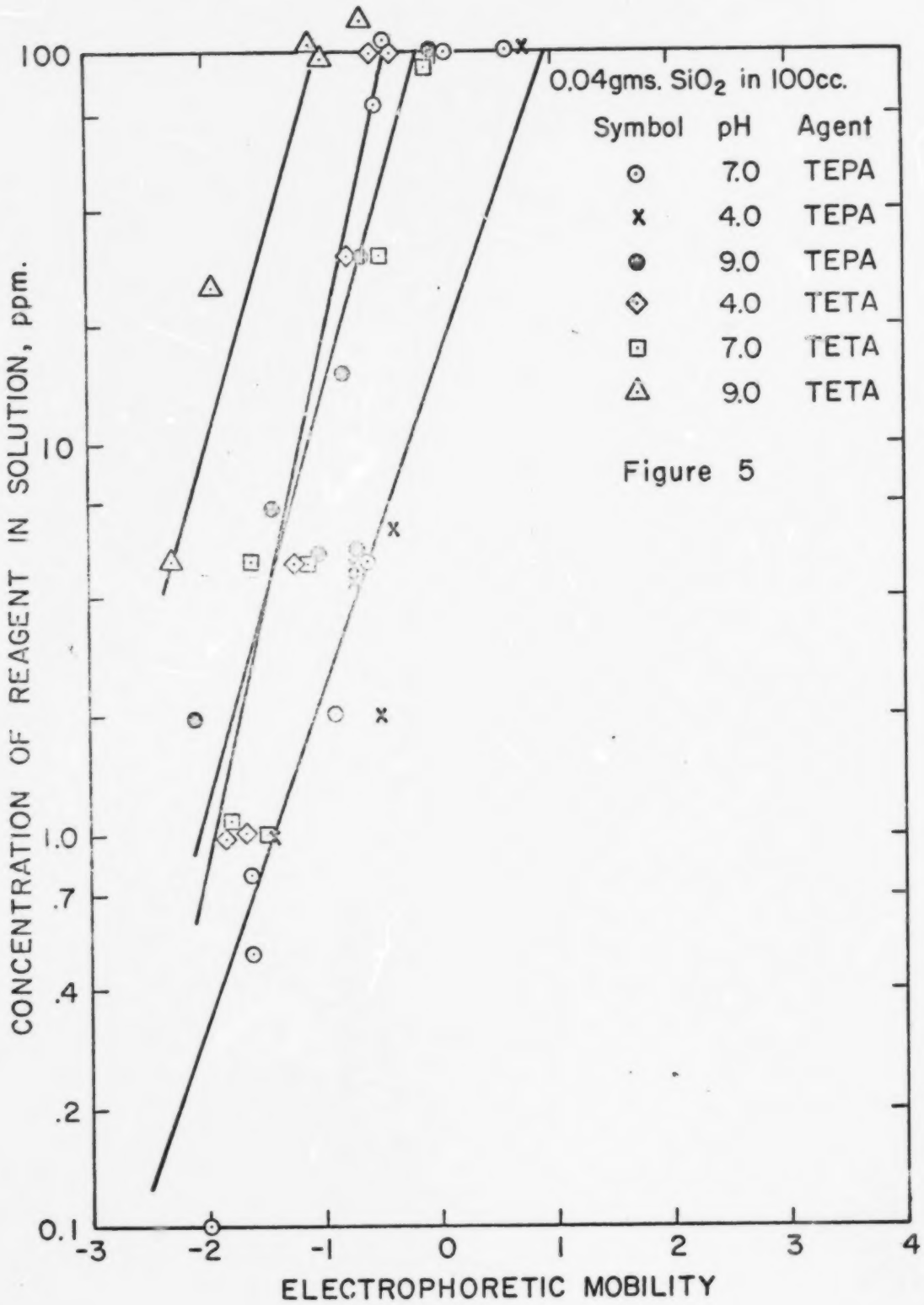
0.04gms. SiO_2 in 100cc.
Symbol pH Agent
⊙ 7.0 TEPA
x 4.0 TEPA
● 9.0 TEPA
◇ 4.0 TETA
⊡ 7.0 TETA
△ 9.0 TETA
CONCENTRATION OF REAGENT IN SOLUTION, ppm.
100
10
1.0
.7
.4
.2
0.1
-3
-2
-1
0
1
2
3
4
ELECTROPHORETIC MOBILITY

Figure 5

FIGURE 6

Effect of Concentration of Cationic Polymer On Electrophoretic Mobility of Crystalline Quartz of "5μ" and "15μ" Nominal Sizes.

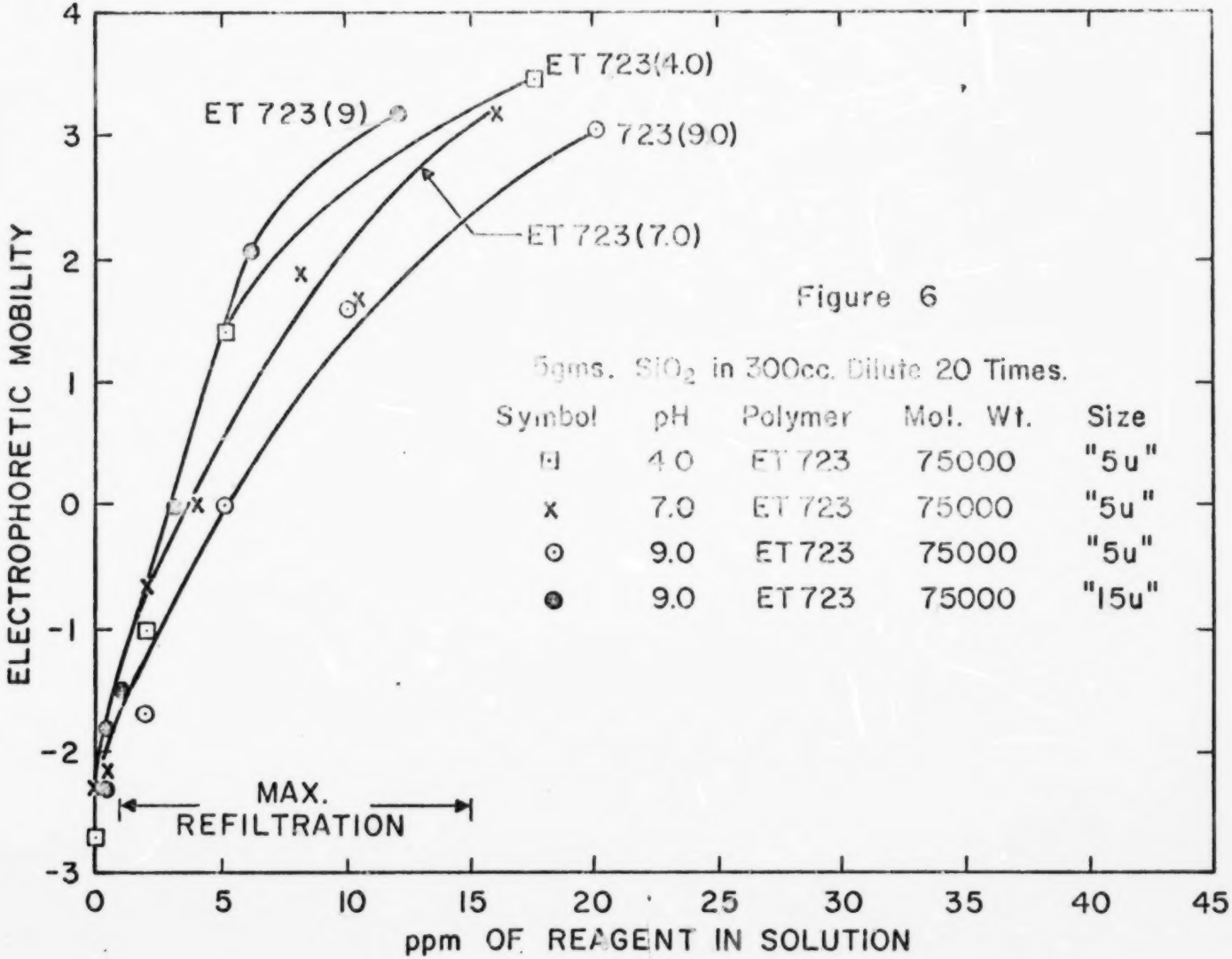

Figure 6

5gms. SiO_2 in 300cc. Dilute 20 Times.

Symbol	pH	Polymer	Mol. Wt.	Size
⊡	4.0	ET 723	75000	"5u"
x	7.0	ET 723	75000	"5u"
⊙	9.0	ET 723	75000	"5u"
●	9.0	ET 723	75000	"15u"

At the same concentration of silica (in g./cc. water), the electrophoretic mobility changes from (-) to (+) at about the concentration of polymer required to first attain maximum filtration rate. Further increase in concentration of polymer increases electrophoretic mobility to +2.0 to +3.0, but the filtration rate remains the same (high) even though the polymer concentration increases some five-fold. For this system the electrophoretic mobility does not have to be close to zero to obtain good filtration and settling.

At high concentrations of polymer and with molecular weights of 25,000 to 75,000 flocculation of the quartz takes place but the filtration becomes very poor, even worse than that on untreated quartz, above a certain critical concentration. Electrophoretic mobility has yet to be determined in this region. Clarity of the supernatant liquid over the coagulated solid is poor, which indicates that the finely dispersed particles are clogging the pores of the filter paper.

IV. Basicity of Polymers

Solutions of the polyalkylamines have been titrated with standard hydrochloric acid to obtain information on their basicity. Unfortunately, the pH titration curves for TEPA and the polyethylene imines are nearly identical in shape and that for TETA is not greatly different so that the effect of basicity of the polymer on adsorption and flocculation cannot be predicted as yet. Work on the modification of the polymer to change its basicity is needed.

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